

CHEMISTRY OF DIFLUORAMINE DERIVATIVES



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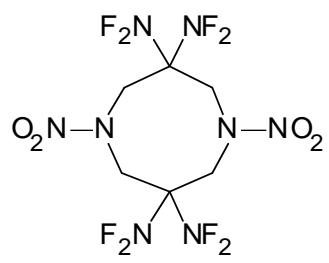
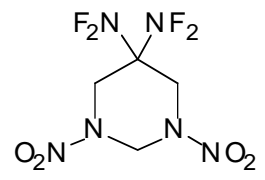
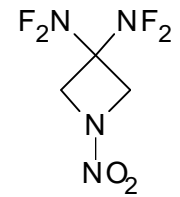
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1. REPORT DATE JUN 1996		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Chemistry of Difluoramine Derivatives				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Weapons Division Research and Technology Division (Code 474220D) China Lake, CA 93555				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 12	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Calculated Performance Characteristics

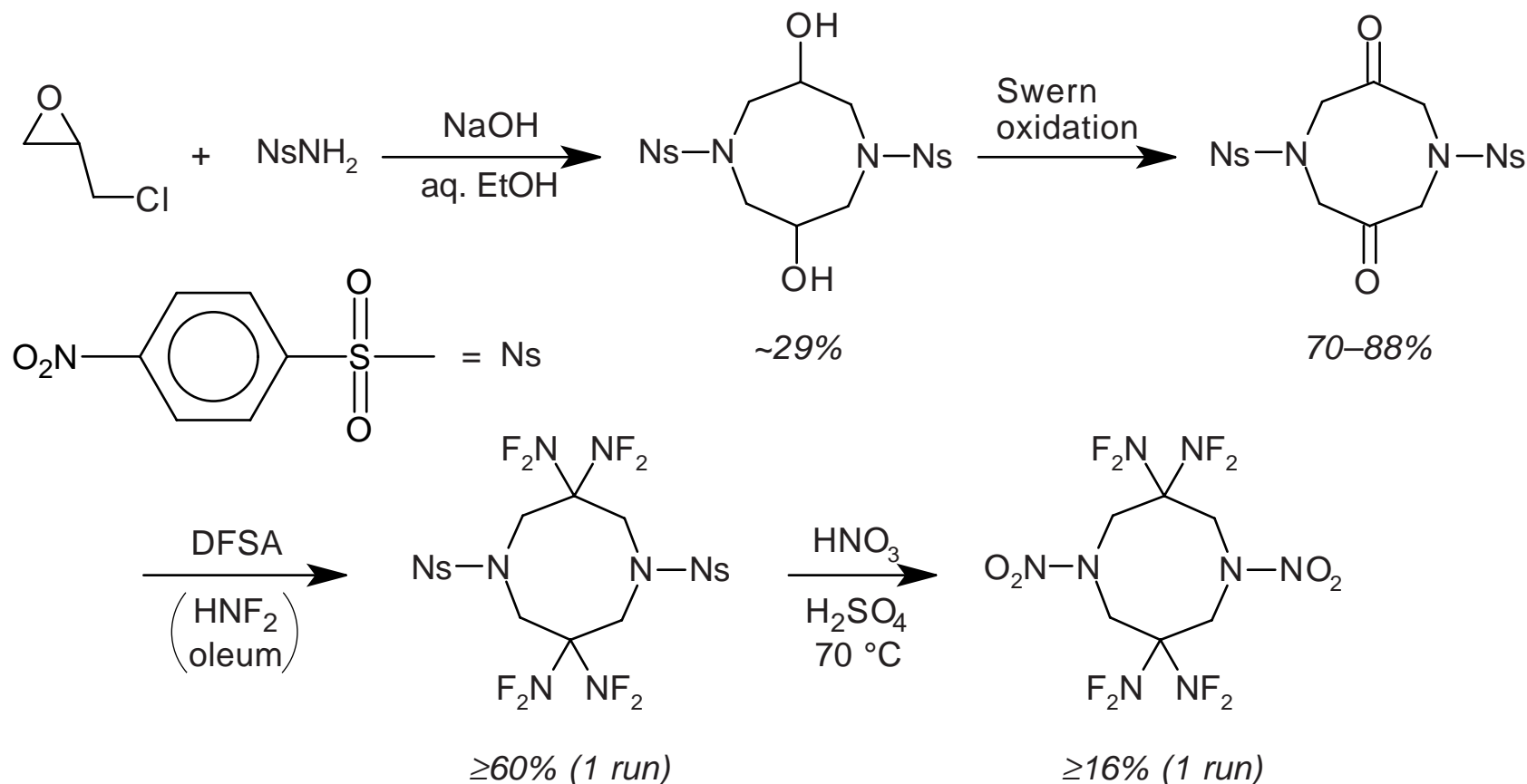
<u>Compound</u>	<u>Density</u> ¹ ρ (g·cm ⁻³) (HMX = 1.894)	<u>Detonation pressure</u> ² P_{CJ} (KBar) (HMX = 390)	<u>Specific impulse</u> ³ I_{sp} (sec) (HMX = 265)
	1.999	474	285
	1.973	444	274
	1.949	443	291

1. Ammon, H.L. (University of Maryland, College Park), personal communication.

2. Adolph, H.G.; Koppes, W.M.; Lawrence, G.W. (Naval Surface Warfare Center, Silver Spring, MD), personal communications.

3. Baroody, E. (Naval Ordnance Station, Indian Head, MD), personal communication.

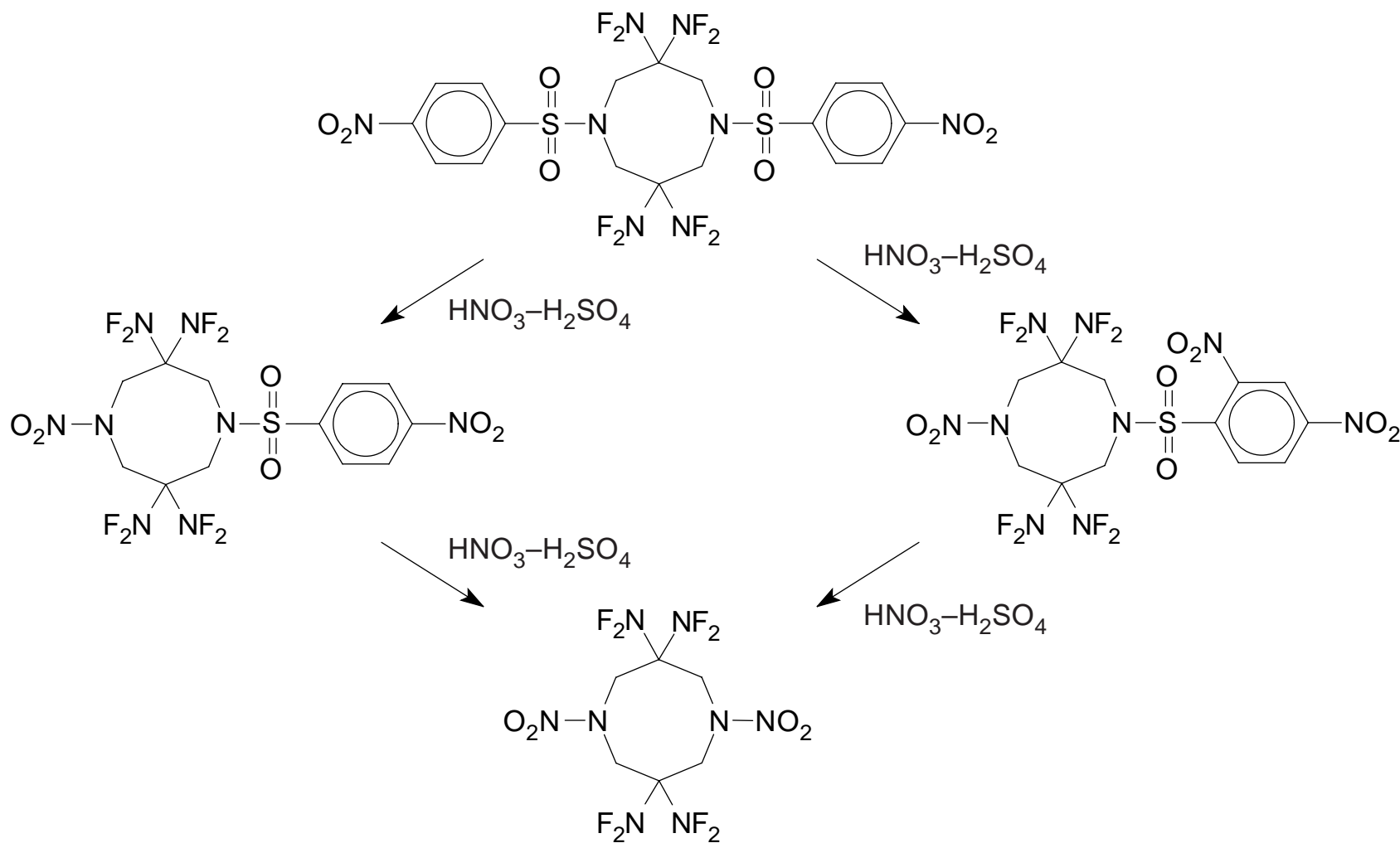
The Best Demonstrated Route to HNFX



Chapman, Kreutzberger & Welker / TPL, Inc.

≡**TPL, Inc.**≡

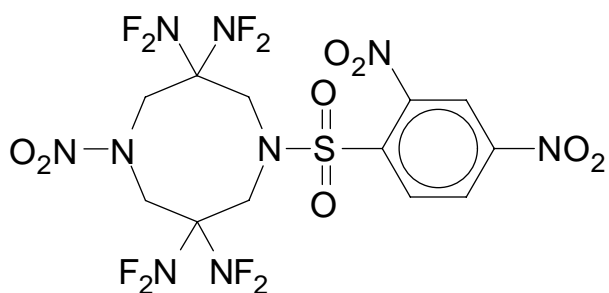
Complications in Nitrolysis



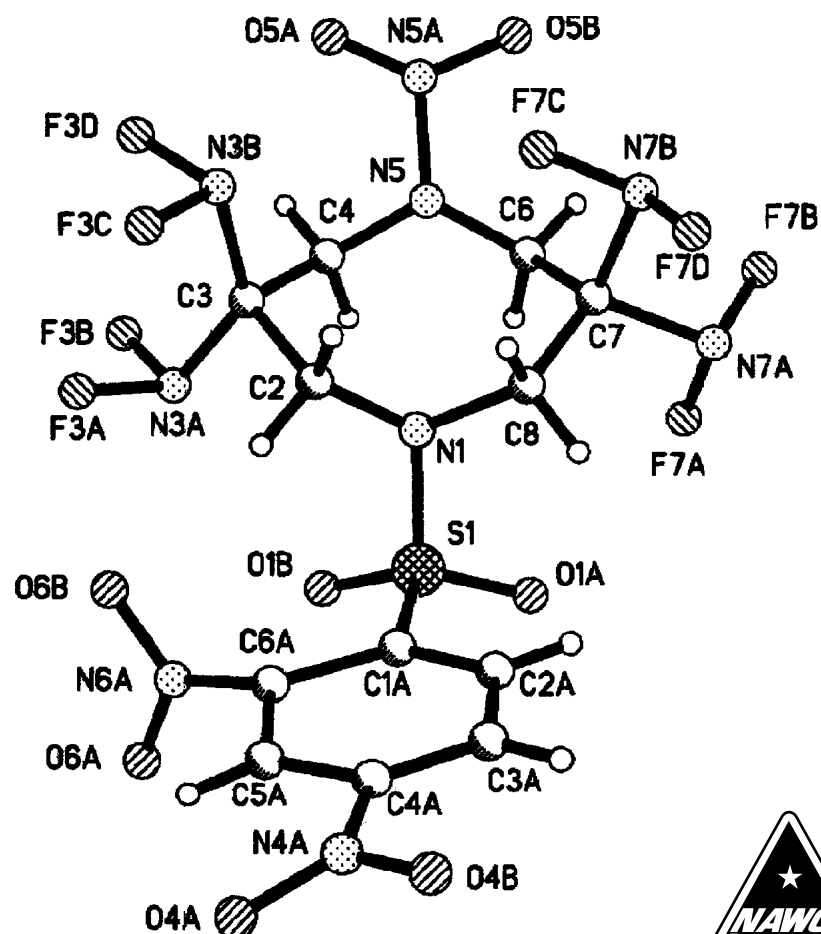
Welker / TPL, Inc.

The Proof

- X-ray analysis (Richard Gilardi, NRL) of a minor impurity crystal in HNFEX



Interestingly,
 $\rho = 1.863$

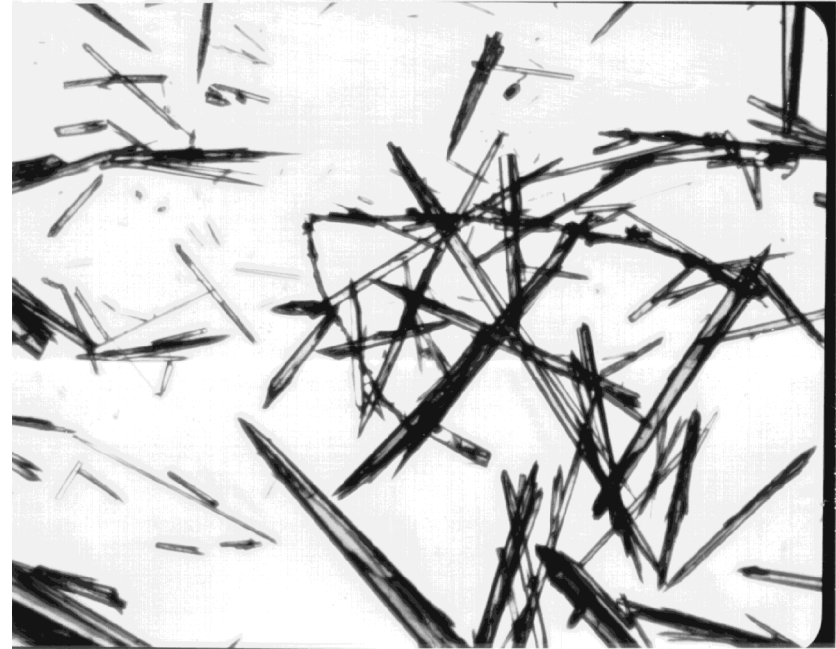
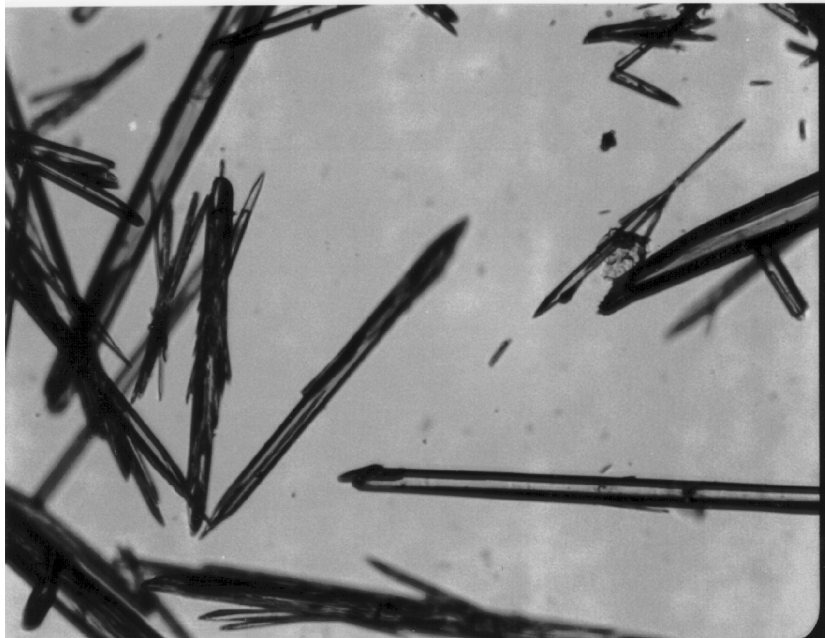


Polymorphism in HNFx

- Original crystal preparation (needles) had solvent channels $\rightarrow \rho = 1.784$ (theor. $\rho = 1.999$)
- New recrystallization from CHCl_3 gives m.p. 216–218 °C without solvent (old m.p. 202~203 °C), but same polymorph!
- New recrystallizations from acetone give *new morphologies*: prisms and plates rather than needles



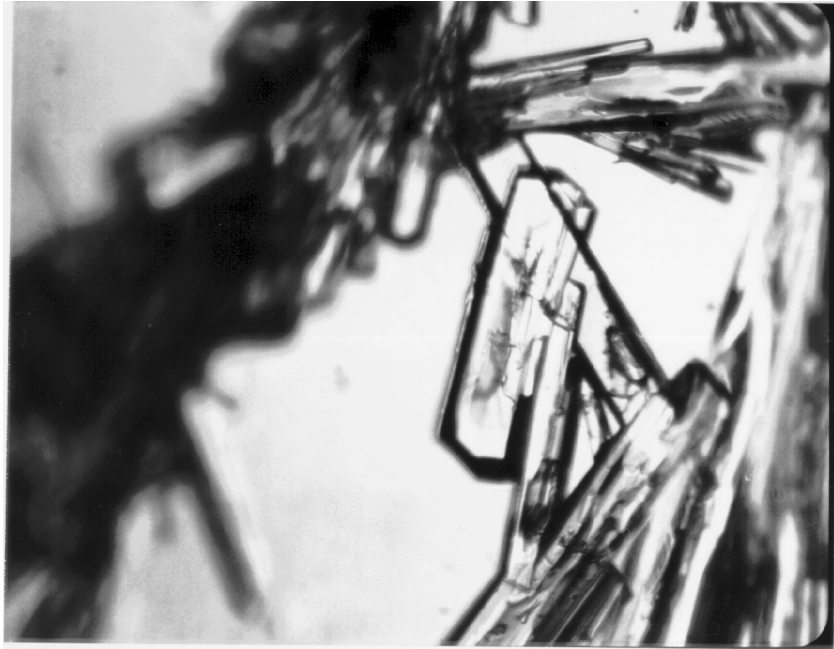
Typical HNFx Needles



~80x



New HNFx Crystal Habits



Prism $0.1 \times 0.02 \times 0.02$ mm




Plate $0.80 \times 0.22 \times 0.02$ mm

- Unit cells measured by Prof. Alan Pinkerton by CCD detector
- But...all crystals are the same polymorph!
- Can you believe it?




HNFX Properties

- M.P. 216–218 °C(dec)
- Readily forms solvent adducts as HMX does
- “Solvent-channel” form (“ α -HNFX”) ρ 1.784
- Comparison of solvent adduct densities:

α -HMX	ρ 1.838		$\Delta\rho \approx 0.25$
HMX·DMF	1.607		
HMX·NMP	1.570		

HNFX·solvent $\rho = 1.784$

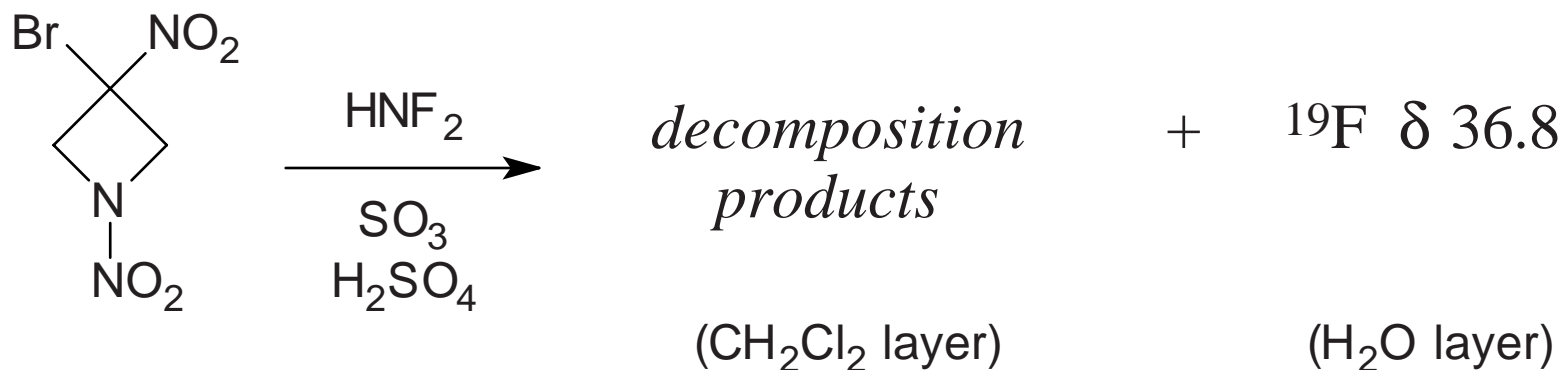
 $\Delta\rho \approx 0.25$

HNFX $\rho \approx 2.03$

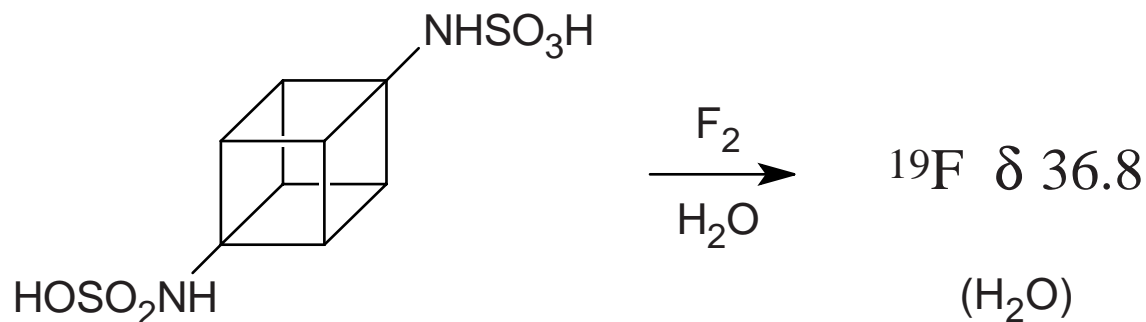
- Impact sensitivity of “ α -HNFX” comparable to PETN



Difluorosulfamic Acid (DFSA): A Recent History



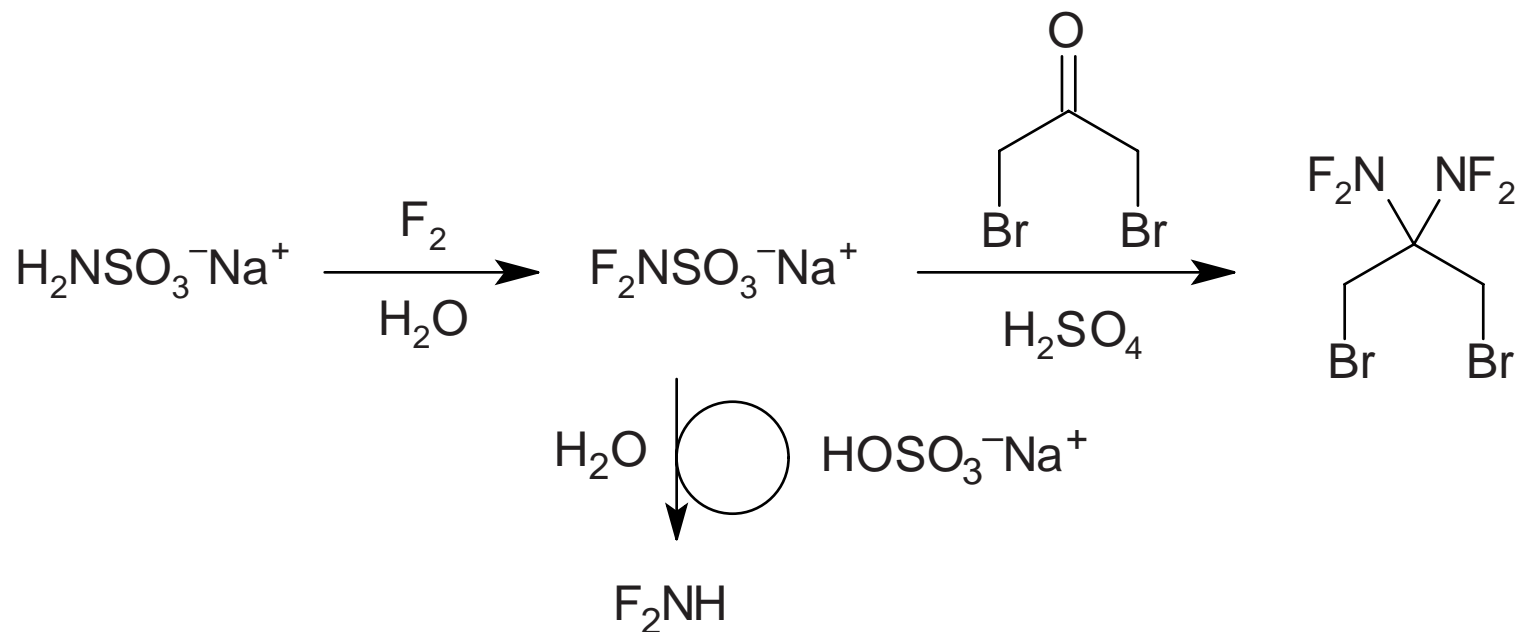
- Chapman, Fluorochem, Jan. 1990



- Archibald, Fluorochem, Jan. 1990

\Rightarrow “Could this be aqueous $\text{F}_2\text{NSO}_3\text{H}$?”

Sodium Difluorosulfamate



- But dilute aqueous $\text{F}_2\text{NSO}_3^-\text{Na}^+$ is stable for weeks at pH 7–8



Acknowledgments

Funding

- Office of Naval Research (Dr. Richard Miller)

